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**QUANTITATIVE VAPOR-PHASE FTIR SPECTRA
OF DIMETHYL METHYLPHOSPHONATE
AND METHYL SALICYLATE**

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13. ABSTRACT (Maximum 200 words) This report summarizes the results of initial tests under Contract No. DAAM01-97-D-0015, Task Order No. 0022. The scope of work was to provide preliminary validation of a system for generating quantitative vapor-phase Fourier transform infrared spectra of CW-related compounds using a saturator cell to generate continuous streams of the compounds. The results of the tests with dimethyl methylphosphonate and methyl salicylate showed that the system appears suitable for the purpose.				
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PREFACE

The work described in this report was authorized under Contract No. DAAM01-97-D-0005, Task Order No. 0022. The work was started in May 2000 and completed in July 2000.

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QUANTITATIVE VAPOR-PHASE FTIR SPECTRA OF DIMETHYL METHYLPHOSPHONATE AND METHYL SALICYLATE

1. SUMMARY

A saturator cell vapor generation system was used to generate continuous streams of dimethyl methylphosphonate (DMMP) and methyl salicylate (MeS), which were supplied to the gas cell of a Fourier transform infrared (FTIR) spectra; and spectra of the compounds were obtained using the apparatus.

2. INTRODUCTION

The present experiments used a saturator cell vapor generator apparatus developed by the U.S. Army Chemical and Biological Center (ECBC) for testing purposes, as well as for measurement of physical properties, including absorption equilibrium and vapor pressure.¹ This device uses a glass tube which a hollow cylindrical ceramic wicking material is fitted. When an organic compound inside the cell is swept by a gas (e.g., nitrogen or air), the gas becomes saturated by the organic compound vapor. At a constant temperature, partial pressure of the vapor will remain constant at a constant total pressure. Previous experimental data have indicated that the concentration of a wide variety of compounds remains constant as the gas flow increases up to at least 500 standard-cm³/min for the vapor generator used in this work.

Initial experiments to assess the vapor pressure of DMMP at ambient conditions had been performed using a mass loss analysis. As long as the system is in dynamic equilibrium, the product concentration should be unaffected by flow rate. However, if the saturator space time is too short to obtain equilibrium, the product concentration will decrease. Care must be taken in quantitative studies to ensure that the generator is operating at the vapor liquid equilibrium (VLE) condition so that the concentration can be calculated. Otherwise, a direct measurement of the actual concentration must be performed. It was demonstrated in previous work that the calculated vapor pressure of DMMP was independent of the actual saturator flow rate.¹

It is also desirable to demonstrate that the quantitative Fourier transform infrared (FTIR) spectra are in a region where Beer's Law applies. Consequently, the experiments described here, which were run 24-30 May 2000, were designed to identify spectral regions where Beer's Law is obeyed and obtain quantitative FTIR spectra in those regions.

3. EXPERIMENTAL PROCEDURES

The vapor generation equipment used for the quantitative infrared (IR) determination included two saturator cells, a Cole-Parmer Polystat® constant

temperature bath (Vernon Hills, IL), two Tylan® mass flow controllers with ranges of 0-1000 standard-cm³/min, and 1/16" o.d. Teflon® tubing fitted with Swagelok® fittings for connecting to the saturator cells.

Spectra were obtained from 4000-650 cm⁻¹ using a Nicolet® Model 560 FTIR at 0.5 cm⁻¹ resolution by coadding 64 scans. The FTIR was outfitted with a 10-m multiple-pass gas cell jacketed to a constant temperature of 30 °C. The FTIR used in the present work has been used previously to obtain quantitative FTIR spectra.² In previous work, vapor streams were supplied to the gas cell using a Kin-Tek® vapor generator (LaMarque, TX). The Kin-Tek has an internal mass flow controller.

Figure 1 is a schematic of the quantitative IR absorption experimental setup. Air from a Whatman® FTIR purge gas generator (Clifton, NJ) was used to supply diluent gas for the experiments. The Whatman zero air generator is capable of supplying air at a dewpoint of -70 °C. Sample lines were plumbed with either 1/4-in. or 1/8-in. o.d. polytetrafluoroethylene (PTFE) tubing. Three-way valves, tees, and cutoff valves were used to switch the flow through the FTIR gas cell between the clean diluent air, for obtaining background spectra and the output of the saturator cell, and for sample spectra. A second mass flow controller, plumbed downstream of the saturator, allowed additional diluent gas to be introduced into the sample stream as needed. The saturator cell was suspended in the constant temperature bath and thermostatted to the desired temperature.

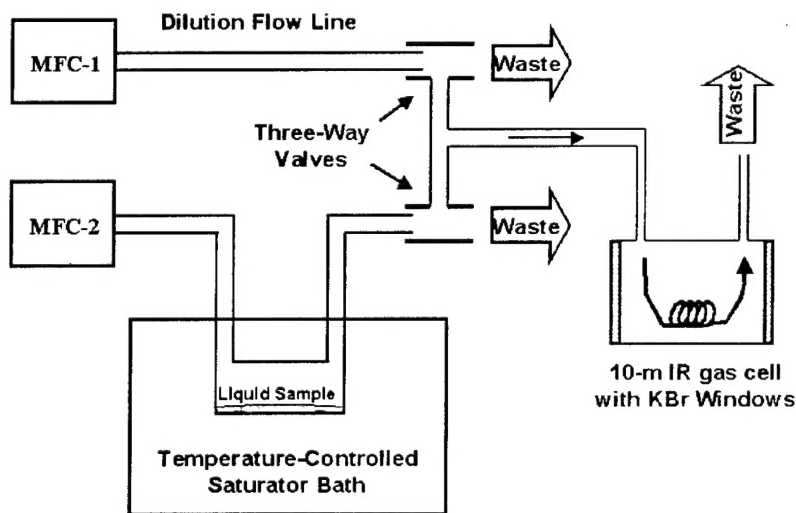


Figure 1. Schematic of Vapor Generator and IR Gas Cell Used to Obtain Infrared Spectra and Assess Vapor Phase Concentration

The DMMP used in the current work was purchased from Aldrich® Chemical Company (Milwaukee, WI) and used without purification in a saturator cell that had previously been used for vapor pressure tests. The original reported purity was 97%. Because most of the impurities in the compound are more volatile than the primary compound, it was presumed that most of these were purged during the conditioning step. Methyl salicylate was purchased from Aldrich Chemical Company at a reported purity of better than 99% and was used as received.

The VLE data in the temperature range of interest had been measured previously for DMMP, who used a similar vapor generation method to that used in this work.¹ In previous work, vapor pressure was measured by tracking the rate of weight loss at several temperatures between -15 and 20 °C. The same method was applied to assess the vapor pressure of MeS at 20 °C. Because that measurement did not correspond to the value obtained by extrapolating literature data,³ a more detailed study was undertaken using a more sensitive purge-and-trap method. This method allows the mass loss rate to be determined using a concentrator-gas chromatography method, previously developed by Buchanan and coworkers, to measure the vapor pressure of VX over the ambient temperature range.^{4,5} The ability to obtain VLE data and generate various vapors using the present methods is crucial to achieving the present objective, because it allows assessment of the vapor-phase concentration present in the cell during acquisition of spectra.

4. RESULTS AND DISCUSSION

Quantitative DMMP FTIR data were measured using a constant temperature bath set to 5 °C. At this temperature, DMMP has a vapor pressure of 24.4 Pa.¹ A flow of 200 standard-cm³/min through the saturator cell was established. After the saturator cell had been stabilized for nearly 4 hr, background spectra were collected with only the dry diluent gas in the 10-m gas cell before flow from the saturator cell was diverted to the gas cell. Spectra were collected at intervals of approximately 10-20 min until successive spectra showed no change in absorbance. Approximately 3 hr were required to stabilize the spectra after the flow of the compound was directed to the gas cell. Thereafter, the flow rate was increased to 400 standard-cm³/min. A spectrum collected 22 min after increasing the flow rate showed no measurable change in absorbance compared to data measured using a saturator flow of 200 standard-cm³/min. This result indicates that the contact time at the higher flow rate was sufficient to achieve VLE. The additional 800 standard-cm³/min of diluent gas was then added downstream of the saturator cell to assess adherence to Beer's Law at the concentration used for these measurements. Analysis of the band at 710.0 cm⁻¹ in the spectrum of the DMMP showed the expected decrease by approximately two-thirds in the absorbance of this band (0.365 before adding the diluent and 0.128 after addition of the diluent gas) as shown in Figure 2. Figure 3 is an FTIR (0.5 cm⁻¹ resolution) spectrum of DMMP obtained at a flow rate of 200 standard-cm³/min. Figure 4 is a similar spectrum obtained using a saturator flow of 400 standard-cm³/min. Figure 5 was

acquired after adding the additional 800 standard-cm³/min of diluent. Figure 6 is a vapor-phase spectrum of DMMP analyzed in the laboratory in 1998 using the Kin-Tek system to generate the vapor. The spectra are expanded to illustrate the fingerprint region between 1400-650 cm⁻¹.

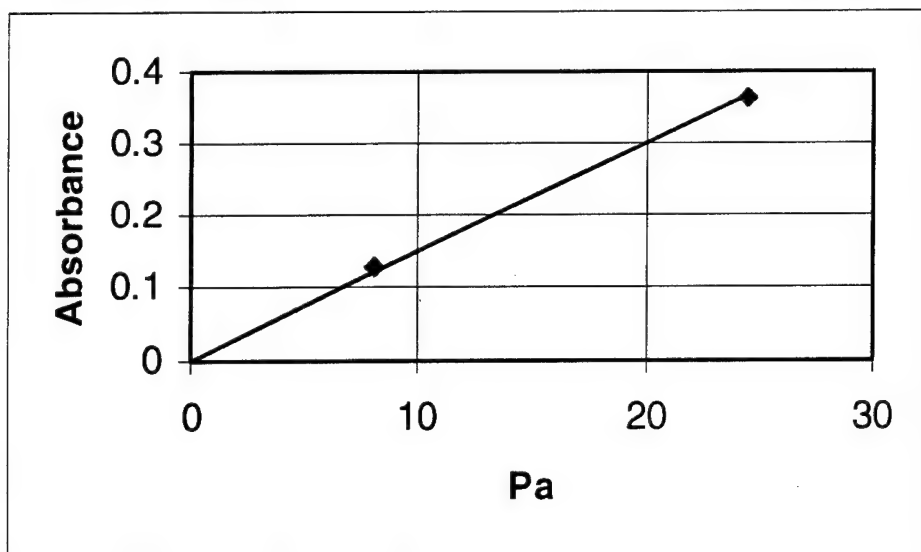


Figure 2. Beer's Law Plot of DMMP Absorption at 710.0 cm⁻¹

Qualitatively, the stronger bands in Figures 3 and 4 appear saturated. The spectrum in Figure 5 is much like the spectrum in Figure 6. The additional sharp bands above 1350 cm⁻¹ (Figure 5) are the result of impure water vapor being introduced into the gas cell through the sample diluent line. The final system will be designed to minimize this interference.

Quantitative IR data for MeS were obtained with the saturator cell operating at 20 °C. The literature correlation indicated a vapor pressure of 2.47 Pa at this temperature.³ Flow through the saturator cell was initially set to 200 standard-cm³/min. Approximately 6 hr were required to stabilize the compound before data collection was initiated. A series of spectra was taken until the absorbances stabilized. The flow was then increased to 400 standard-cm³/min, with no change in absorbance.

On the following afternoon, additional spectra were obtained with the flow through the saturator cell at 400 standard-cm³/min. The spectra showed no significant change in absorbance from the previous day. An additional 800 standard-cm³/min of diluent was then added downstream from the saturator cell and spectra were taken until the absorbance stabilized. Using the band at 1095.1 cm⁻¹ as a reference, the absorbance decreased as expected. The magnitude of the decrease obeyed Beer's Law going from 0.531 to 0.189 (Figure 7).

Figure 8 is a spectrum of methyl salicylate taken on day 2 with the flow through the saturator cell at 400 standard-cm³/min. Figure 9 is a spectrum taken after an additional 800 standard-cm³/min of diluent was added to the stream. Figure 10 is a

vapor-phase spectrum of the compound obtained in 1998 using the Kin-Tek system to generate the vapor stream.

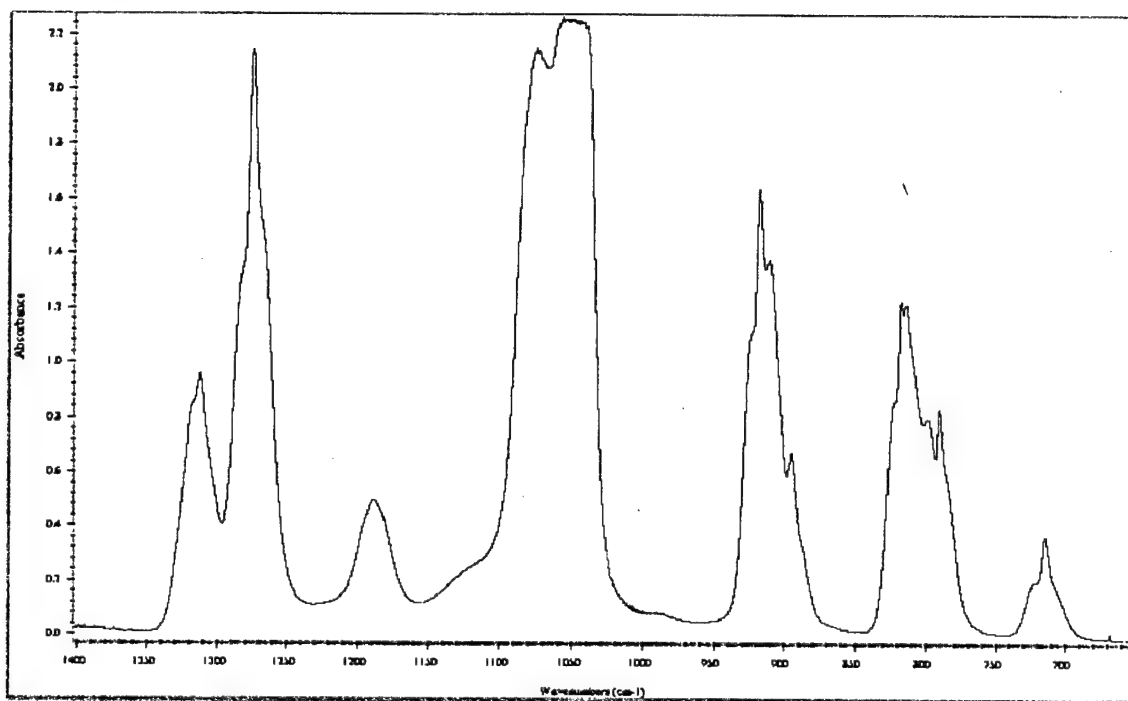


Figure 3. Spectrum of DMMP at 200 Standard-cm³/min Flow

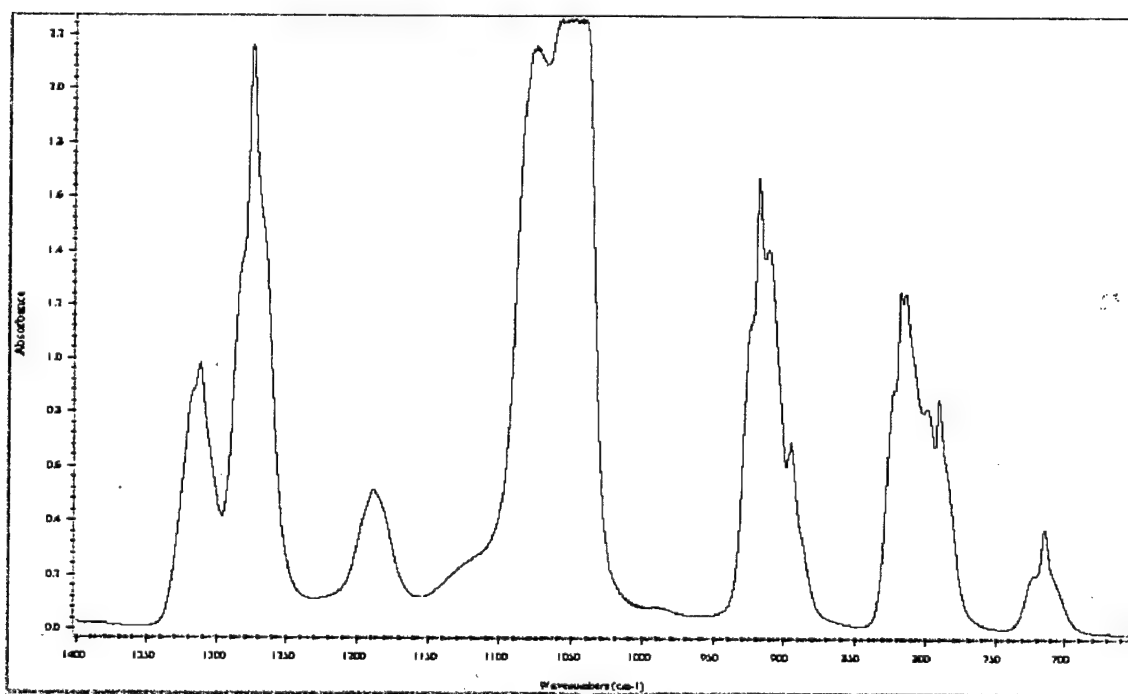
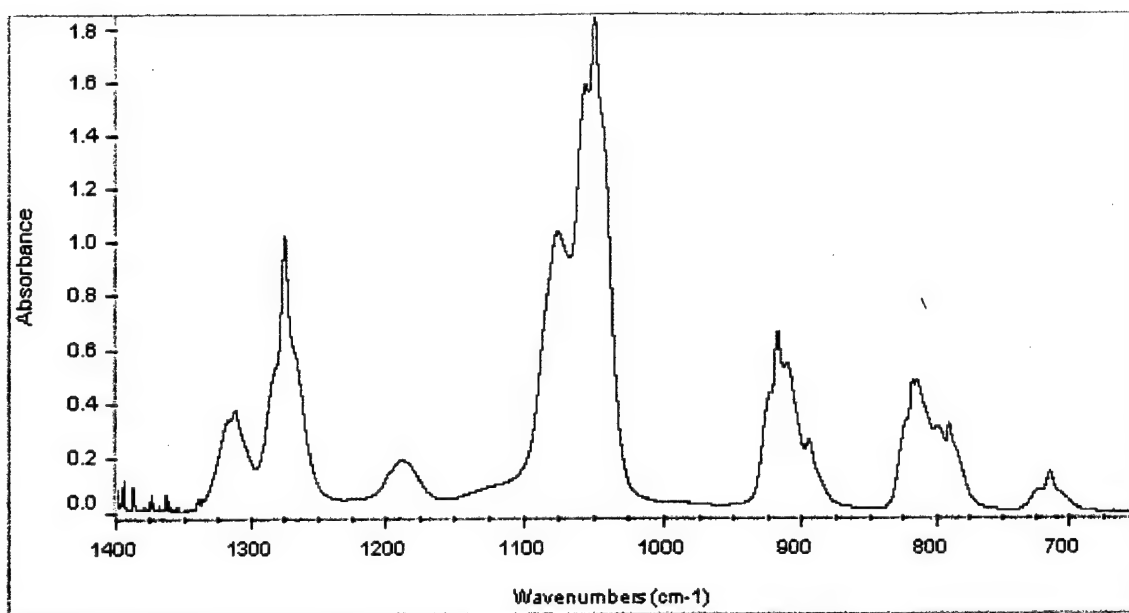


Figure 4. Spectrum of DMMP at 400 Standard-cm³/min Flow



**Figure 5. Spectrum of DMMP at 1200 Standard-cm³/min Flow
(400 Standard-cm³/min Through Saturator)**

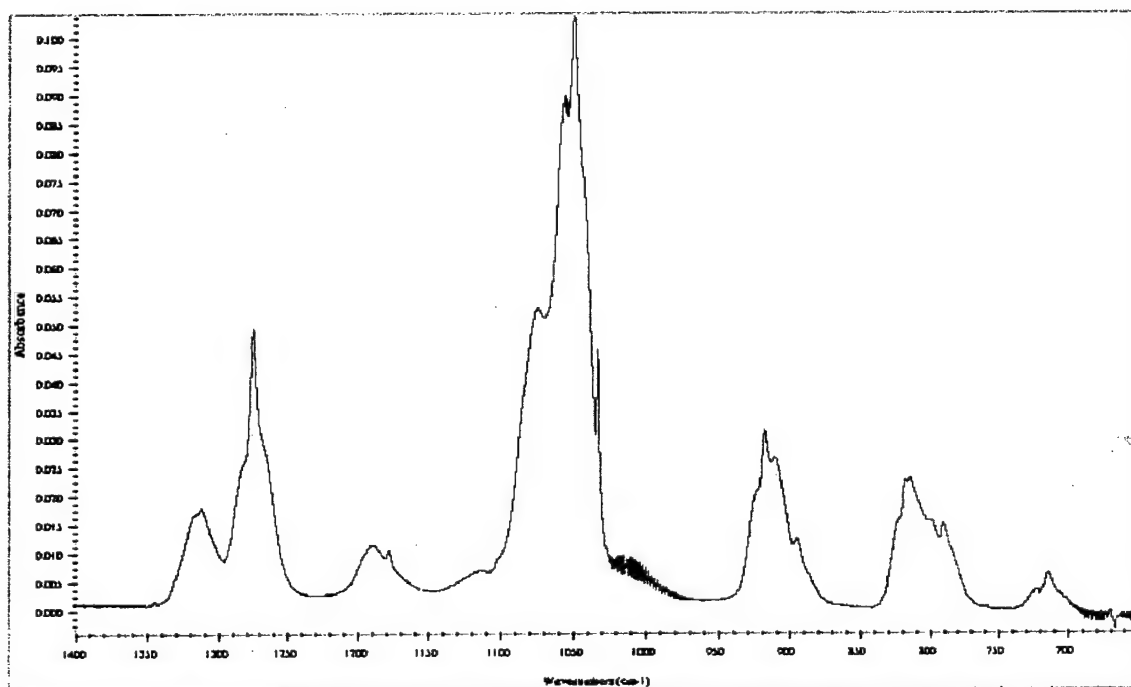


Figure 6: Vapor-Phase Spectrum of DMMP from Kin-Tek Generator System

Qualitatively, the three MeS FTIR spectra are similar. The primary differences are in the spectrum in Figure 9, which shows the strong, sharp bands from water vapor as the additional diluent gas was introduced into the sample stream.

The concentrations of DMMP and MeS generated during the recent experiments were approximately an order of magnitude higher than those obtained in 1998. Caution should be applied, therefore, in comparing the spectra quantitatively. Additionally, the FTIR gas cell was operated at a temperature 20 ° higher in 1998, which could have caused some band broadening during the prior work. Furthermore, the vapor concentrations in the 1998 work were determined using only thermal desorption-gas chromatography, which was inherently less precise than the gravimetric method used in the current study.

Notwithstanding the cautions that should be applied, if the 1998 FTIR data for DMMP are extrapolated, the current FTIR data appear consistent with the vapor pressure obtained by Tevault, et al.¹ In the case of the MeS, the FTIR spectra obtained in 1998 appear to show that the concentration of MeS in the more recent experiments is higher than would have been expected on the basis of Daubert's (extrapolated) vapor pressure correlation. This further indicates that our vapor pressure data for this compound appear to be closer to the actual value. To explore this hypothesis further, the vapor pressure of MeS has been measured in the range of -10 to 20 °C. The result of that series of measurements, which were obtained using the method previously used to determine VX vapor pressure over the ambient temperature range, indicate a VLE value of 9.4 Pa for MeS at 20 °C.* This value was confirmed using a simple mass loss method at 20 °C.

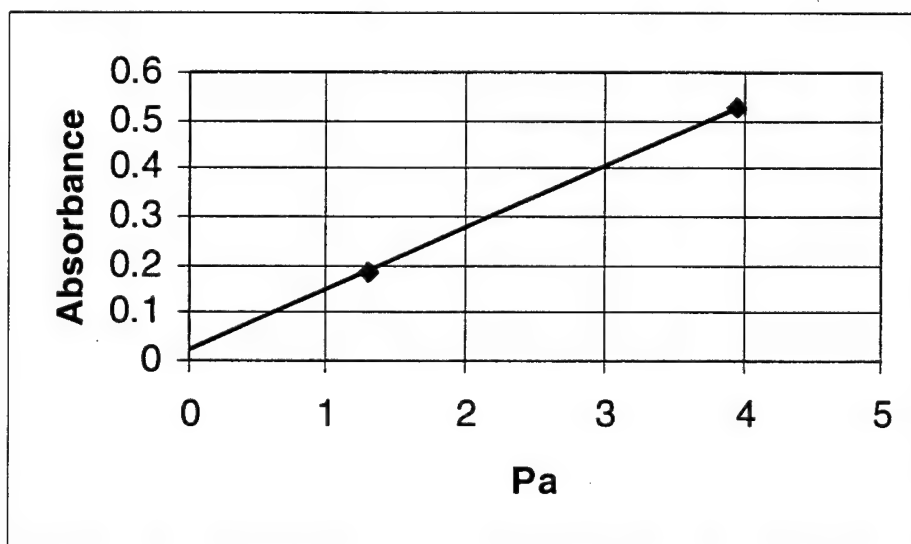


Figure 7. Beer's Law Plot of MeS Absorption at 1095 cm⁻¹

*Matson, K., Buettner, L.C., and Tevault, D.E., U.S. Army Edgewood Chemical Biological Center, February 2001, unpublished data.

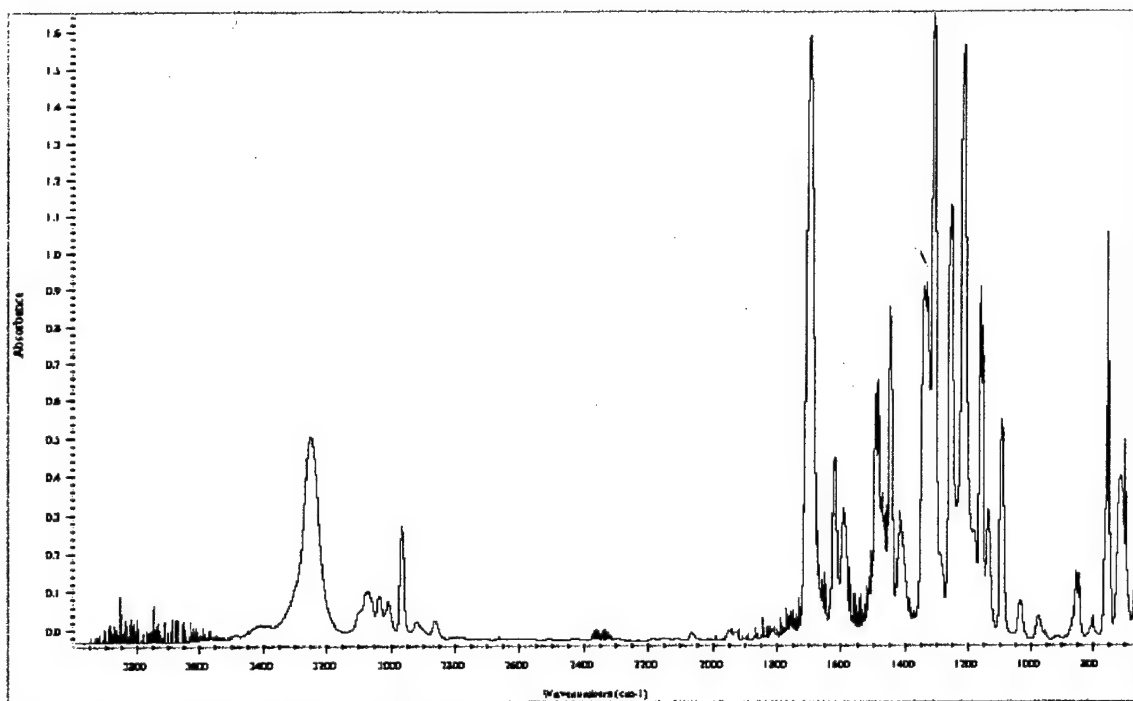


Figure 8. Spectrum of Methyl Salicylate at 400 Standard-cm³/min Flow

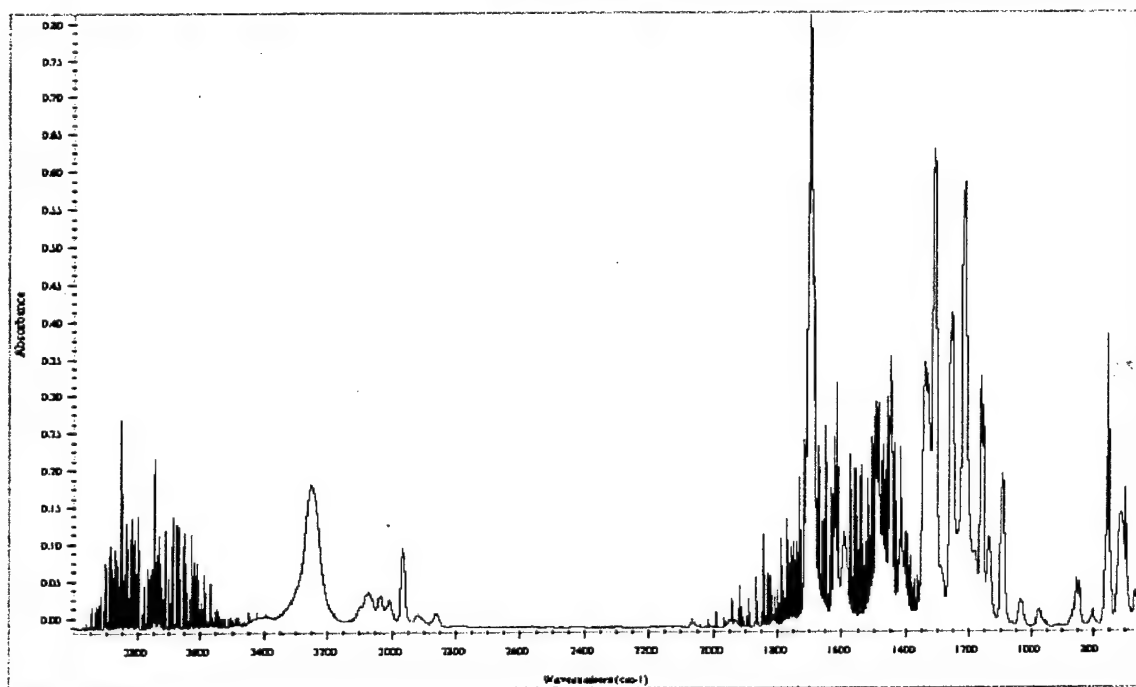


Figure 9. Spectrum of Methyl Salicylate at 1200 Standard-cm³/min Total Flow (400 Standard-cm³/min Through Saturator)

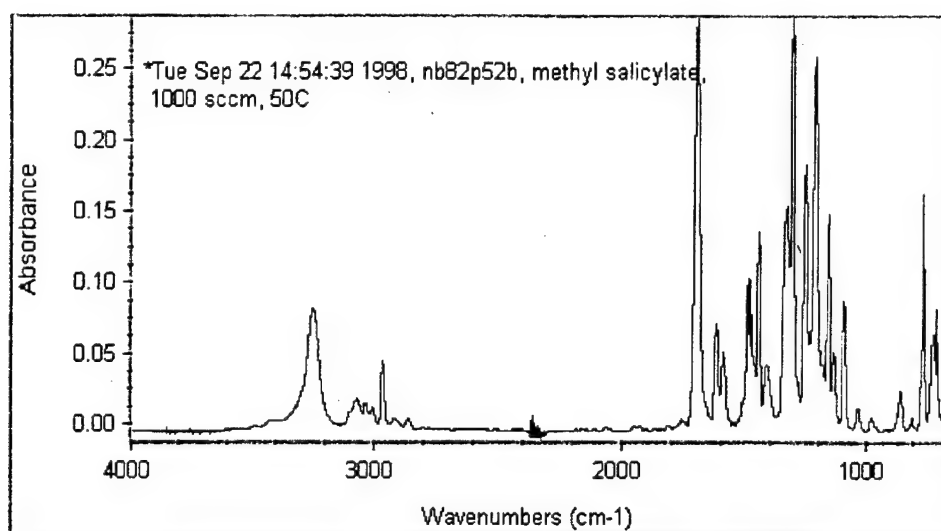


Figure 10. Vapor-phase Infrared Spectrum of Methyl Salicylate from Kin-Tek Generator System

5. CONCLUSIONS

A design for the quantitative Fourier transform infrared (FTIR) laboratory, using the saturator cell to generate the vapor streams, has been demonstrated in the present series of experiments. This method appears to be suitable for generating quantitative vapor-phase spectra of compounds with a significant range of volatility. The lower limit, using this method, will depend on the sample vapor pressure and operating temperature, as well as absorption coefficients and path length of the infrared cell. Based upon the methyl salicylate data presented here, materials with similar absorptivities should be detectable at pressures below 0.01 Pa (100 ppb), which corresponds to a temperature near room temperature for VX. Future quantitative FTIR data will provide absorbances at a minimum of five partial pressures.

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ACRONYMS AND ABBREVIATIONS

cm ⁻¹	Reciprocal centimeters, wavenumbers
DMMP	Dimethyl methyl phosphonate
ECBC	Edgewood Chemical and Biological Center
FTIR	Fourier transform infrared
MeS	Methyl salicylate
o.d.	Outside diameter
Pa	Pascal
PTFE	Polytetrafluoroethylene
cm ³ /min	Standard cubic centimeters per minute
VLE	Vapor-liquid equilibrium
VX	O-Ethyl-S-(2-diisopropylamino)ethyl methylphosphonothioate

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